

Study of Methyl Rotations in Octamethyl-POSS

An experimental investigation using High Flux
Backscattering Spectrometer at NCNR

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HFBS Team

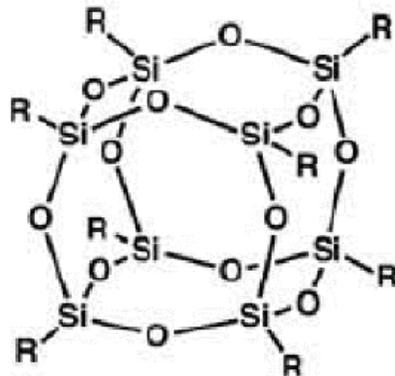
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Abstract

In this experiment, we will use elastic and quasi-elastic neutron scattering to examine the methyl rotations in octamethyl-POSS. The goal of this hands-on measurement is to gain an understanding and appreciation of backscattering spectroscopy, get practical experience in obtaining the elastic and quasi-elastic data, reduce, analyze and interpret a set of these data.

I. Introduction

Polyoligosilsesquioxanes (POSS) are molecules composed of silicon-oxygen cage in which Si atoms occupy the corners of a cube and oxygen atoms are located on the edges. Each Si atom is bonded to three oxygen atoms but may have any one of a wide variety of potential ligands attached to the fourth position. The choice of ligands provides many useful properties, including selective solubility in organic or aqueous solvents, the ability to be dispersed in a number of polymers, and specific chemical reactivity that can be used to directly incorporate the POSS molecule into the polymer backbones or side groups. POSS can also be used as a small, perfectly monodisperse nanoparticle with diameter of the order of a few nm (see below).



The influence of choice of ligand on POSS molecule can be seen through their sample form at room temperature. In pure state, POSS exists as amorphous solid, crystalline solids and even as liquid depending upon the ligand attached to Si atoms. Larger and flexible ligands tend to discourage crystallization and lower the POSS melting temperature while smaller ligands generally enhance crystallization in POSS molecules [1]. The smallest possible POSS would be where R in the above is replaced with simple hydrogen.

In this experiment, we will investigate motions in octamethyl-POSS (M-POSS) where R is substituted with a methyl group using quasi-elastic neutron scattering. M-POSS is a crystalline material at room temperature and appears white. M-POSS is known to sublime at around 473K. Therefore, we intend to perform all measurements at lower temperatures.

II. Why study M-POSS using Neutron Backscattering?

As stated above, POSS molecules have a wide variety of applications including their use as nanoparticles for polymer nanocomposites. For such applications, knowledge of dynamical modes is desirable, as ligands are known to facilitate solubility and good nanoparticle dispersion in polymer seems to be related with ligand dynamics. As the ligand conformational energy barriers generally have significant intermolecular

component, we expect the ligand dynamics and vibrational transition energies to be sensitive to the interactions between the POSS molecules and the polymer chains.

Why neutron backscattering - the answer has to do with the suitability of the length and time scales associated with the dynamics in these systems. As we all know, momentum transfer Q is inversely related with length scales under investigation. So, we can consider Q as the power of our microscope that we are using to probe the dynamical properties of M-POSS. The Q values covered by HFBS ($0.25\text{\AA}^{-1} - 1.8\text{\AA}^{-1}$) correspond to length scales of 35\AA to 4\AA and are suitable to study methyl group rotations.

Furthermore, by varying the contrast between the structural units or molecular groups, complex systems may be selectively studied. In particular, the large contrast achieved by isotopic substitution of hydrogen by deuterium constitutes the most powerful tool for deciphering complex structures and dynamic processes in these materials. To give you an idea here are some of the incoherent (and coherent) scattering cross sections for common elements: H: 80.5 (1.75) barns, D: 2.0 (5.5) barns, C: 0.0 (5.5) barns, O: 0.0 (4.2) barns and Si: 0.0 (2.16). As the incoherent cross section of hydrogen is much larger, the total scattering observed in a quasi-elastic neutron scattering (QENS) experiment will be dominated heavily by incoherent scattering from hydrogen in the sample.

III. Experimental Plan and Sample Environment

M-POSS is a crystalline material which can be obtained commercially. This particular sample was bought from Hybrid Plastics and used as is. About 0.4g powder was put in an aluminum pouch and rolled to make a thin film of M-POSS. The film is then rolled into an annulus (cylinder) and inserted into the sample can, which was sealed with indium under helium to have an excellent heat transfer. The annular geometry was selected to minimize the amount of corrections necessary in the data reduction. If the sample is too thick, then a significant number of the neutrons may get absorbed. This *self-shielding* depends on the absorption cross-section of the sample as well as the geometry. For an annular geometry where the neutron sees only a thin portion of the sample, the corrections are negligible. Another concern when determining sample design is minimization of *multiple scattering*. In an ideal neutron scattering measurement, we would like for the neutron to scatter once within the sample before reaching the detector. In practice, the neutrons can undergo several scattering events within the sample and/or be absorbed by the sample. The number of events increases with the thickness of the sample illuminated by the beam. One often used rule-of-thumb is to design sample geometry where 90% of the incident neutrons are transmitted in the forward direction. This is a good compromise between signal and the effects of multiple scattering. Such a sample is usually referred to as a *10% scatterer*. Using the known scattering and absorption cross-sections for M-POSS and the geometry, one can calculate the desired thickness or the amount of material. For M-POSS in an annular cell the approximate sample for 90% transmission in the forward direction is *0.25 mm*.

Q: How many times does the beam go through the sample before

reaching the detectors?

The answer to the question posed above can have important consequences for your experiment. If the beam passes through the sample twice (for instance) and the sample has an appreciable neutron absorption cross-section, then the intensity at the detectors will be lower than if the beam had only passed once through the sample. Additionally, a beam which passes twice through a strongly scattering sample can produce an energy-dependent background. For more details on these points, see Appendix A.

The sample can will be placed in a top loading closed-cycle refrigerator capable of reaching a base temperature of 4 K. The measurements performed here will cover a temperature range of 4K -298K. We will use a low-T sample sticks to cover the entire temperature range. We will start with so-called “Fixed window scan” and scan the intensities from 298K to 4K. Resolution measurements will be made in quasi-elastic mode at 4K followed by a number of quasi-elastic scans at different temperatures determined by fixed window scan.

IV. Modes of Spectrometer and Data Reduction Details

We can use HFBS spectrometer in two different modes to extract the dynamical features of the sample under investigation.

A. Fixed Window Scans:

For reactor based neutron backscattering spectrometers, “Fixed window scans” or “elastic scans” are very powerful for getting a fast overview of the dynamics of a system and are often the starting point for quasi-elastic measurements. In this mode, we choose to count the neutrons with fixed initial and final wave vectors which results in analyzing neutrons scattered within a fixed energy window. To do so, we stop the moving monochromator (see below) and then change the external parameters like temperature and pressure and record the intensity. We can even assign a time scale to fixed window scans based on the instrumental resolution. In our case, assuming a FWHM of about $0.8\mu\text{eV}$, the slower limit would correspond to about 10ns. Dynamic processes on a time scale slower than the instrumental resolution are not resolved and thus are counted within the "elastic window". Faster motions of scattering particles can be resolved and will induce an energy loss or gain of the scattered neutrons, which then are no longer reflected by the analyzers to the detectors. One observes a decrease of the elastic window intensity as function of increasing temperature. Therefore, elastic or fixed window scans give a quick overview of the onset of motions faster than the time scale corresponding to the energy resolution (~ 10 ns) and therefore, can be used to choose suitable temperatures for dynamic measurements.

B. Quasi-elastic Neutron Scattering:

The HFBS spectrometer is configured in an *inverse scattering geometry*. This means that the energy of the neutron incident on the sample is varied while the final energy of the neutrons reaching the detectors is fixed.

A summary of the basic principle of operation of HFBS is outlined below (for more details on the instrument including a schematic see Appendix B)

1. The “white” beam of neutrons produced by the reactor is velocity selected to yield neutrons that have energies around the desired energy of 2.08 meV. These neutrons are further focused in energy by a rotating phase space transform chopper and scattered towards the Doppler monochromator. The energy focused neutrons are backscattered from the Doppler monochromator thus selecting incident neutron energies, E_i , dependent upon the speed of the monochromator when reflected. While the Doppler is at rest, only neutrons with energies of 2.08 meV are backscattered from the monochromator. This is due to the lattice spacing of the Si hexagons that tile the surface of the monochromator.
2. The reflected neutrons from monochromator interact with the sample and are scattered from the sample with a distribution of energies.
3. Only neutrons with a particular scattered energy, E_f , reflect from the analyzer array into the detectors. Identical Si hexagons comprise the analyzer system, thus the backscattered neutrons all have energies of 2.08 meV. The energy transfer imparted on the sample is defined as $E = E_i - E_f$.
4. Neutrons scattered from the sample in a particular direction backscatter from particular analyzers and are counted by one of the 16 detectors. This direction corresponds to the scattering angle, 2θ .

Q: What is the energy range of the neutrons incident on the sample, E_i ?

Note: this next section will be conveyed using energy, wavelength and velocity. These values are generally constant for HFBS; the neutrons that reach the detectors have energies of 2.08 meV, wavelengths of 6.27 Å and velocities of 630.8 m/s.

Given the scattering angle, 2θ , and energy transfer, E , we may calculate the magnitude of the momentum transfer delivered to the sample, Q . Kinematical arguments lead to the following relationship between 2θ , E , E_i , and Q :

$$\frac{\hbar^2 Q^2}{2m_n} = 2E_i - E - 2\sqrt{E_i(E_i - E)} \cos(2\theta)$$

where m_n is the mass of the neutron and \hbar is Planck's constant.

The data acquisition system records the number of detector counts as a function of initial neutron velocity, v_i , where v_i is related to the instantaneous monochromator velocity, v_m , and the Bragg velocity of the neutrons with velocity 630 m/s, v_B , via $v_i = v_B + v_m$. The energy transfer to the sample, due to a Doppler shift of the neutron energies, is given by,

$$E = 2E_B \left(\frac{v_m}{v_B} \right) + E_B \left(\frac{v_m}{v_B} \right)^2$$

where E_B is the Bragg energy of neutrons with wavelength 6.27 Å, is calculated and written to the raw data file. This calculation is done using an encoded Doppler drive that provides information as to the acceleration as a function of position. The energy change is derived from this acceleration. Note that the motion of the monochromator is time-dependent, allowing the variation of E_i necessary to an inverse geometry spectrometer.

Q: Can you think of a way to change the incident neutron energies without moving monochromator?

The raw data measured is recorded as $N(2\theta_j, E_k) = N_{jk}$, the number of neutrons detected in detector j (at scattering angle corresponding to $2\theta_j$) with an energy transfer to sample of E_k . The quantity which reflects the dynamics of the scattering system most directly is $S(Q, E = \hbar\omega)$, the dynamic structure factor. What we measure, N_{jk} , is closely related to the partial differential cross-section, $d^2\sigma/d\Omega dE$. This can be written in terms of the various instrument-dependent parameters and the number of counts received in the detectors,

$$\left[\frac{d^2\sigma}{d\Omega dE} \right]_{j,k} = \frac{N_{j,k}}{\eta(E_f)} \frac{A\eta(FC)}{N(FC)} \gamma_j \frac{1}{\rho_N V} \frac{1}{\Delta\Omega_j} \frac{1}{\Delta E}$$

where,

$\left(\frac{A\eta(FC)}{N(FC)} \right)$: the monitor normalization of incident beam area (A) times the beam monitor efficiency ($\eta(FC)$) divided by the number of counts received by the beam monitor. (FC) indicates the type of detector, a fission chamber.

$\frac{\gamma_j}{\eta(E_f)}$: the vanadium normalization of the detector intensity with the intensity scaling factor γ_j divided by the efficiency of the detector.

ρ_N : number density of scatterers in the sample

V : volume of sample illuminated by the beam

ΔE : energy channel width or binning of the dynamic range

$\Delta\Omega_j$: solid angle subtended by detector or analyzer angular coverage

We can obtain the dynamic structure function, $S(Q,E)$, using the first Born approximation (i.e. a single scattering event dominates the response of the scattering system) via

$$S(Q, E) = \frac{4\pi}{\sigma} \frac{k_i}{k_f} \frac{d^2\sigma}{d\Omega dE}$$

where,

σ : scattering cross-section

k_i : incident neutron wave vector

k_f : final neutron wave vector

Note that for a sample in thermal equilibrium, the *detailed balance condition* is satisfied,

$$S(Q, -E) = e^{-\frac{E}{kT}} S(Q, E)$$

where E is the sample energy gain. This condition is a technical way of saying that it is more likely that a sample will give energy to the neutron when the sample is at a high temperature as compared to when the sample is at a low temperature.

V. Understanding Quasi-elastic Neutron Spectra and Models

The neutron intensity after correction gives the experimental scattering function $S_{\text{exp}}(Q, \omega)$ as a function of energy transfer ($E=\hbar\omega$). The theoretical scattering function $S(Q, \omega)$ which gives the dynamics of a general system in a quasielastic neutron scattering experiment is given by [2]

$$S_{\text{theo}}(Q, \omega) = f^* \{p_1(Q)\delta(\omega) + p_2 S_{\text{QE}}(Q, \omega)\} + S_{\text{IN}}(Q, \omega)$$

where f is just a scaling factor that describes the attenuation of scattering intensity as a result of temperature variation, p_1 and p_2 represents the elastic and quasi-elastic contribution to total scattering function. $\delta(\omega)$ is Delta function corresponding to zero frequency. $S_{\text{QE}}(Q, \omega)$ and $S_{\text{IN}}(Q, \omega)$ are the quasi-elastic and inelastic incoherent scattering functions respectively. $S_{\text{IN}}(Q, \omega)$ can also be used to describe the processes that are much faster than one's instrument frequency window in the form of a flat background.

The measured neutron spectra is always resolution broadened and therefore, it is important to remember that the above eq has to be convoluted with experimental resolution function before it can be fitted to experimental measured scattering function. The resolution function is the slowest possible scattering function that can be measured at a given instrument. For more details on resolution function, please see appendix C. We will use DAVE software to analyze fixed window scan and quasi-elastic data. More

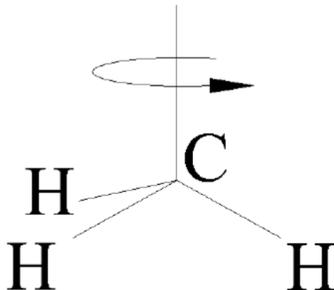
details about DAVE software can be found at: <http://www.ncnr.nist.gov/dave> **As for scattering function, hereafter, we will talk only about theoretical scattering function.**

Q: Can we measure resolution function using our own sample for this experiment?

As noted above, hydrogenated sample of M-POSS will scatter incoherently and almost all the intensity will be incoherent in nature coming from 8 methyl groups. The incoherent intensity reveals the incoherent scattering function, $S_{inc}(Q, \omega)$, that is related via Fourier transformations to the intermediate incoherent scattering function, $S_{inc}(Q, t)$, and with the self-part of the Van Hove correlation function, $G_{self}(r, t)$. In the classical limit, $G_{self}(r, t)$ is the probability of a given nucleus being at distance r from the position where it was located at a time t before. Thus, incoherent scattering looks at correlations between the positions of the same nucleus at different times. Therefore, in backscattering measurements, we observe a given particle's self correlation function $S(Q, t)$ in frequency domain and with its time (frequency) evolution, we can track how the molecule is diffusing in space (through Q dependence) and time.

Theory of methyl group rotation:

At very low temperatures, all diffusional motions are frozen in solids and only short range vibrations are present in which molecules vibrate around a fixed center of mass. A methyl group is best described by a pyramid composed of three hydrogen atoms at the base and a carbon atom at the apex with H-H distance which is usually around 1.5 \AA (see below). It has been established that below 30K or so if any quasi-elastic broadening occurs in the data over elastic line this normally corresponds to quantum rotational tunneling of methyl groups. In polymer system where a more complex dynamics occur broadening can be observed even below 30K, however this is not the case for solids. In the higher temperature range say 60K and above a more classic rotational motion appears as crossover from quantum to classic rotations occurs around 50K or so. The classic hopping rates of the hydrogens in the methyl groups can be determined by the Q - and temperature dependence of quasi-elastic broadening of the elastic line over resolution. For more details on quantum tunneling please see Ref.3.



In the classic model, the interaction between methyl groups and surrounding environment is described by the single particle model. In this model methyl group is typically treated as rigid rotor whose rotation is hindered or influenced by the surrounding. The potential that hinders the reorientation depends on a singular coordinate θ which represents the

rotation angle of the methyl group with respect to its fixed environment. The total rotational potential energy can be determined using the symmetry of the methyl group as well as of the environment.

A realistic model for methyl group rotation would be a 3-fold function as

$$V(\theta) = \frac{V_3}{2}(1 - \cos 3\theta)$$

where V_3 denotes the amplitude of the potential. The maxima of $V(\theta)$ represents the height of the barrier for the hopping process. This potential also determines the quantized torsional or librational levels.

Q. Can we observe torsional and librational peaks in our experiment? Hint: V_3

We can use the torsional transition energies to determine the barrier height separating the equivalent methyl group orientations. If the torsional potential is composed of the 3-fold term as given above then the energy levels are given by the solutions of Schrodinger eq:

$$H\psi_n(\theta) = E_n\psi_n(\theta)$$

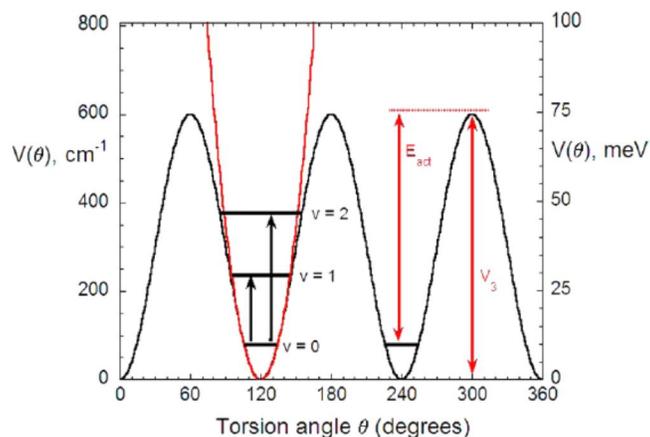
where H is given by

$$H = -\frac{\hbar^2}{2I} \frac{d^2}{d\theta^2} + \frac{V_3}{2}(1 - \cos 3\theta)$$

and the free rotor wave functions are given by

$$\psi_n(\theta) = \frac{1}{\sqrt{2\pi}} e^{\pm in\theta}$$

Here I is the methyl rotational constant. The eq. above can be solved numerically and the eigenvalues for the rotational energy levels and resulting transition energies can be used to determine the value of the barrier height. This procedure yields V_3 to be 74.4meV [4]. A plot of $V(\theta)$ against torsion angle can be seen below:

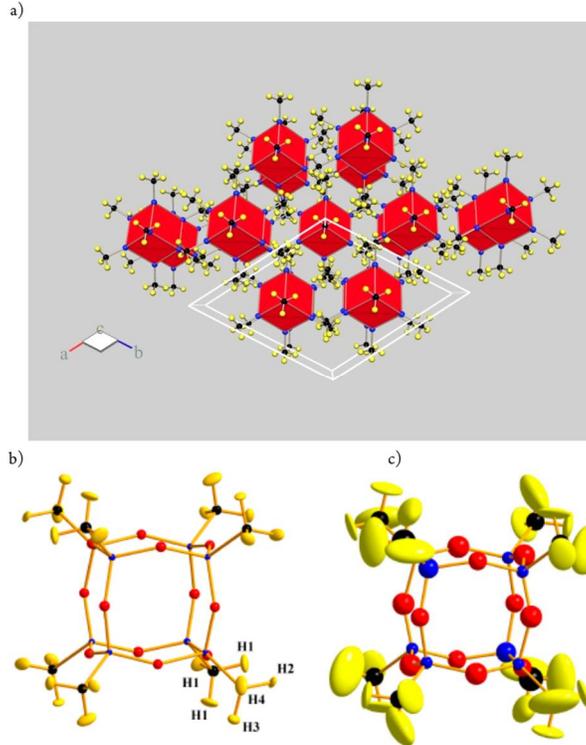


The activation energy is defined as the energy difference between the ground state torsional state and the top of the barrier. This way activation energy is always less than the barrier height. Also note these torsional energy levels are 3-fold degenerate. The degeneracy will be lifted by tunneling matrix elements between the potential energy wells to yield two levels for each torsional level. The tunnel splitting for the ground state is also given by above calculation and yields $0.1 \mu\text{eV}$.

Q. Do we expect to see any tunneling in this experiment?

Symmetry of Methyl Groups:

Neutron diffraction and X-ray has been used to determine crystal structure of M-POSS [4]. At 300K, M-POSS adopts a rhombohedral crystal structure with space group R-3, as shown in the figure below. Lattice constants are $a=b=12.50\text{\AA}$ and $c=13.09\text{\AA}$. There are 3 M-POSS molecules per crystallographic unit cell. As the unit cell has 3 M-POSS molecules understanding the symmetry of methyl groups in a molecule of M-POSS is important. Two of the eight methyl groups in an M-POSS molecule in the crystal lie on the hexagonal c axis and therefore have C_3 symmetry while the other 6 methyl groups do not lie on symmetry axes or planes and therefore have C_1 symmetry instead. These two methyl groups can be seen below where H_1 atoms belong to the one with C_3 symmetry while H_2 , H_3 and H_4 belong to the one with C_1 symmetry.



Q: Do you expect any influence of symmetry on methyl rotations via neutron spectra?

In the above Fig., (b) shows molecular structure at 12K while (c) shows the same at 300K. Notice the large hydrogen atom anisotropic displacement due to the presence of large amplitude torsional motions of methyl group.

Modeling of Dynamic Scattering function:

Methyl group rotations can be modelled by a simple Lorentzian function which is given as follows:

$$L(Q, \omega) = \frac{\Gamma(Q)}{\hbar^2 \omega^2 + \Gamma^2(Q)}$$

Therefore, the total function to be fitted would be

$$S(Q, \omega) = f * [p_1 \delta(\omega) + p_2 L(Q, \omega)] \otimes R(Q, \omega)$$

where the key parameters are p_1 , p_2 and $\Gamma(Q)$. In the above eq. p_1 and p_2 represent fraction of elastic and quasi-elastic signal while $\Gamma(Q)$ represent the full width at half maximum (FWHM) of quasi-elastic broadening.

The Elastic Incoherent Structure Factor (EISF):

Quasi-elastic neutron scattering provides direct information about the geometry of the motion through Q dependence of the data. In order to access information about the motion, we need to calculate what is called EISF. The EISF is the fraction of the elastic signal over total signal which can be defined as

$$A_0(Q) = \frac{p_1(Q)}{p_1(Q) + p_2(Q)}$$

The variation of EISF as a function of Q can provide us the exact geometry of methyl rotations. Symmetric methyl groups rotate around their C₃ axes, where the hydrogen atoms for each methyl group are located on 3 sites equally spaced on a circle. The EISF has been calculated for a number of models[1]. The EISF for this model is

$$A_{3sites}(Q) = \frac{1 + 2j_0(Qr)}{3}$$

where r is the jump distance separating the hydrogen atoms undergoing the rotational diffusion and j₀ is the spherical Bessel function of zeroth order. The above eq. can also be written as

$$A_{3sites}(Q) = \frac{1}{3} \left[1 + 2 \frac{\text{Sin}(Qr)}{Qr} \right]$$

Q: Do you expect any temperature dependence of EISF?

Q dependence of Full width at half maximum:

The Q dependence of FWHM can be used to figure out how hydrogen atoms are moving in space. For example, in the simplest case of Brownian diffusion FWHM varies as Q² and proportionality constant is simply diffusion coefficient. In case of polymers, where chain connectivity “prevents” simple diffusion of hydrogen atoms, Q dependence is slightly more complex and found to be stronger than Q². In case of geometrical confinement liquids are found to show weak Q dependence and tend to follow Q^γ where γ is usually between zero and 2. A Q independent FWHM typically refers to a confined motion or geometrically restrictive motion on corresponding length scale.

Temperature Dependence of FWHM

The rotational diffusion of methyl groups can be treated as thermally activated process that is best described by a simple Arrhenius eq.

$$\Gamma(T) = \Gamma_0 e^{-E/kT}$$

Where Γ_0 is the attempt frequency and E is the rotational activation energy. The above eq. means if logarithm of FWHM is plotted against inverse of temperature, it should yield a simple linear plot. Typically methyl group rotation leads to activation energies that fall in the range of 50mev-80mev.

Attempt frequency in the above eq. is another very important parameter and can give crucial information about the nature of the motion involved. In case of typical methyl rotation, attempt frequencies are generally found to be in the order of 2-5 meV. These values typically mean methyl rotation occurs nearly perfectly without any distortion or coupling.

Q. Can you calculate expected activation energy of methyl rotation using potential energy plot?

VI. References:

- 1] D. B. Cordes, P. D. Lickiss, F. Rataboul, "Recent Developments in the Chemistry of Cubic Polyhedral Silsesquioxanes", Chem. Rev., 2010, 110, 2081.
- 2] M. Bee, *Quasi-elastic Neutron Scattering*, Adam Hilgor, Bristol (1988).
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Appendix A

Effects of the Sample Geometry on Self Shielding and Multiple Scattering

One must consider a number of issues when determining appropriate sample geometry. A naïve philosophy in designing sample geometry is to make the sample as big as possible in order to obtain as many scattering events in the shortest possible time. Unfortunately optimization of the experiment is not as simple as this. Sample design involves a careful consideration of the composition of the sample in terms of its scattering and absorption cross-sections.

In an inverse geometry spectrometer like HFBS where the beam passes through the sample twice one must consider *self-shielding* effects which reduce the intensity received at the detectors via absorption. In general absorption in the sample is proportional to the neutron wavelength. On a backscattering spectrometer using Si(111), $E_i = 2.08$ meV, $\lambda = 6.27$ Å, which results in the cross section for absorption being 3.5 times larger than for thermal neutrons with 1.8 Å.

In order to understand the extent to which you have to correct for multiple scattering/self-shielding it is important to know how strong a scatterer/absorber your sample is. The transmission in the forward direction ($2\theta = 0$) is often calculated and expressed in terms of a percentage of the incident beam that is scattered/absorbed. For instance, a flat plate sample with total scattering cross-section, $\sigma_{\text{tot}} = \sigma_{\text{inc}} + \sigma_{\text{coh}}$, and absorption cross-section, σ_{abs} , will have a scattering and absorption determined by

$$\text{scattering} = 1 - \exp\left(-\frac{\mu_s d}{\sin(\pi - 2\theta)}\right) \quad (\text{flat plate}) \quad \text{A1}$$

$$\text{absorption} = 1 - \exp\left(-\frac{\mu_{\text{abs}} d}{\sin(\pi - 2\theta)}\right) \quad (\text{flat plate}) \quad \text{A2}$$

where 2θ is the angle of orientation of the slab with respect to the incident beam direction, d is the thickness of the slab sample, and μ is the scattering coefficient (inverse scattering length in cm^{-1}) determined by

$$\mu_s = N_A \sigma_{\text{tot}} \rho / M \quad \text{A3}$$

$$\mu_{\text{abs}} = N_A \sigma_{\text{abs}} \rho / M \quad \text{A4}$$

where N_A is Avogadro's number ($6.022 \times 10^{23} \text{ mole}^{-1}$), ρ is the mass density of the sample material (in g/cc), and M is the molecular weight of the sample in g/mol. On the other hand an annular sample cell has a scattering/absorption in the forward direction determined by

$$\text{scattering} = 1 - \exp(-\pi \mu_s d) \quad (\text{annular cell}) \quad \text{A5}$$

$$absorption = 1 - \exp(-\pi\mu_{abs}d)$$

(annular cell)

A6

where the inverse scattering absorption lengths are calculated as described above (eqs. A3 and A4) and d is the wall thickness of the annular sample. Equations (A5) and (A6) are good approximations for the cases where $\exp(-\pi\mu d) > 80\%$.

We illustrate the self-shielding corrections for a vanadium sample ($\sigma_s(1.8 \text{ \AA}) = 5.10$ barn and $\sigma_{abs}(1.8 \text{ \AA}) = 5.08$ barn [A1]) for two different geometries: a flat plate and an annular sample. The intensity in the detectors is very sensitive to the thickness of the sample as well as its geometry. If we assume these two geometries for the same amount of scattering (5%, 10%, and 20% scatterers respectively as calculated via (A1) and (A5)) and assume that the samples are completely illuminated by the incident beam then we obtain the results displayed in figure A1. The corrected intensity is obtained using $I_{corr}(2\theta, E) = I_{obs}(2\theta, E)/A_{ssc}$ where $I_{obs}(2\theta, E)$ is the observed intensity. It is quite clear that there is a much stronger angle dependence for the correction factor of the slab geometry whereas the corrections are much less for the annular cell. Furthermore, an evaluation of the correction factor is impossible near the orientation angle, 130° in the present example, for the slab geometry. Therefore it is advantageous to use an annular geometry for backscattering. Note that, because the beam goes through the sample twice on HFBS, the sample transmission due to the presence of absorption must be squared.

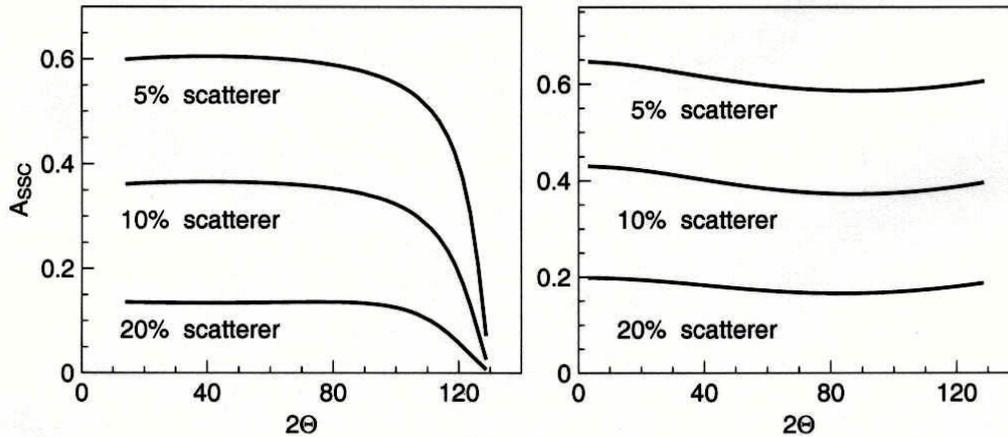


Fig.A1: Scattering angle dependence of the self-shielding correction factor for (a) flat plate whose normal is oriented 130 degrees with respect to incident beam direction and (b) an annular sample geometry.

When one increases the thickness of the sample for a system with a medium absorption cross-section the intensity will not significantly increase but the effects of multiple scattering will certainly be enhanced. Corrections for multiple scattering are not trivial and, for many systems in which the scattering function is not known a priori, may not be possible at all.

Figure A2 illustrates the effects that multiple scattering can have on a system, in this case viscous glycerol. This sample was measured on the IN10 backscattering spectrometer at the ILL at a temperature where the structural relaxation (viscous flow) is on the time scale of the instrument (0.1–1 ns). There is a clear broadening of the lineshape with increasing Q (FWHM $\sim Q^2$) due to the dynamics of the system. However at $Q = 0.19 \text{ \AA}^{-1}$ structural relaxation cannot be resolved because it is too slow at this small Q . The effective broadening in the wings is entirely due to multiple scattering.

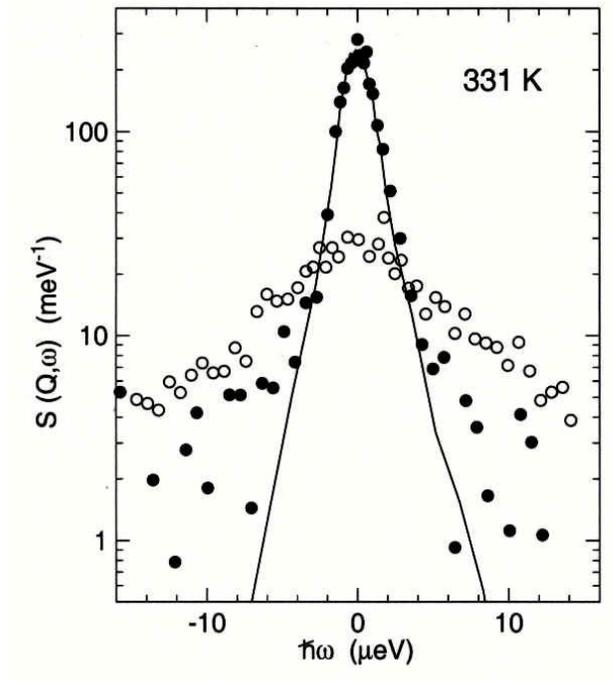


Fig.A2: Scattering intensity of viscous glycerol taken on the IN10 backscattering instrument illustrating the effects of multiple scattering on $S(Q, \omega)$. Solid line represents the instrumental resolution, open symbols are data taken at $Q=1.4 \text{ \AA}^{-1}$, and the closed symbols are data taken at $Q=0.19 \text{ \AA}^{-1}$ [A2].

References

[A1]. V.F.Sears, Neutron News **3**, 26 (1992)

[A2]. J. Wuttke et al., Phys. Rev. E **54**, 5364 (1996)

Appendix B

Instrument Characteristics for the High Flux Backscattering Spectrometer

(<http://www.ncnr.nist.gov/instruments/hfbs>)

Si (111) analyzers covering 20% of 4π steradians

Si (111) monochromator 52 cm wide \times 28 cm tall

$$\lambda = 6.27 \text{ \AA}$$

$$E_f = 2.08 \text{ meV}$$

$$v_n = 630 \text{ m/s}$$

16 ^3He detectors covering $14^\circ < 2\theta < 121^\circ$

Dynamic range:

$$-36 \text{ \mu eV} < \Delta E < 36 \text{ \mu eV}$$

$$0.25 \text{ \AA}^{-1} < Q_{\text{EL}} < 1.75 \text{ \AA}^{-1}$$

$$\tau \approx 0.05 - 10 \text{ ns}$$

Instrumental resolution:

$$\delta E < 1 \text{ \mu eV (FWHM)}$$

$$\delta Q = 0.1 \text{ \AA}^{-1} - 0.2 \text{ \AA}^{-1}$$

Flux at sample:

$$\Phi \approx 1.4 \times 10^5 \text{ n/cm}^2/\text{s}$$

Beam size at sample:

$$2.8 \text{ cm} \times 2.8 \text{ cm}$$

Signal to noise:

400:1 for vanadium foil (10% scatterer)

Sample environment:

Furnace (300 K – 1700 K)

Closed cycle refrigerator (5 K – 325 K)

Closed cycle refrigerator (50 K – 600 K)

Orange cryostat (1.5 K – 300 K)

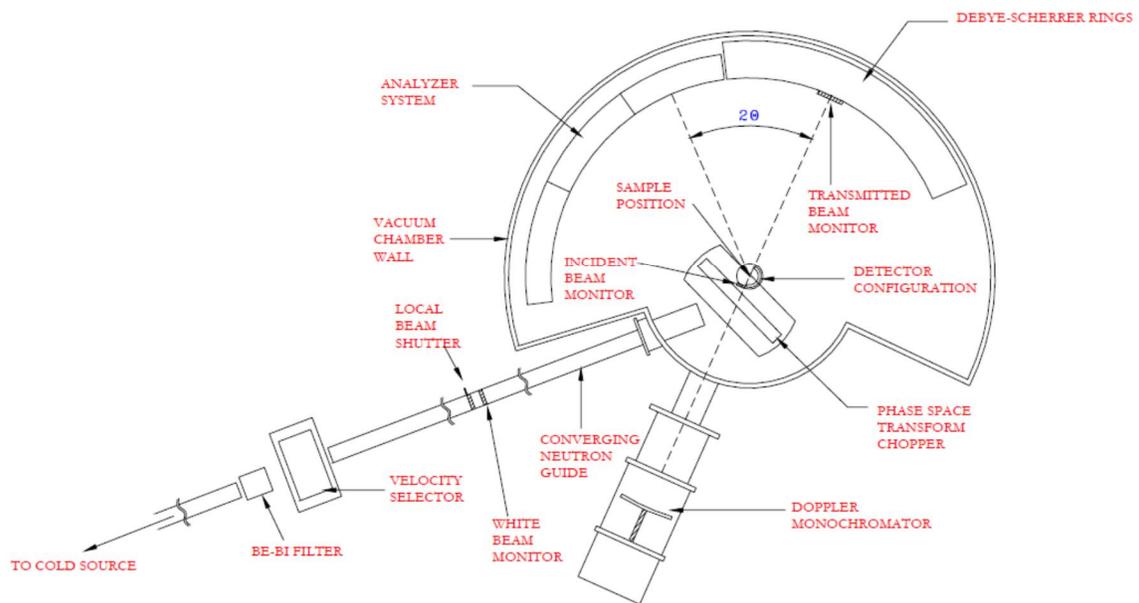


Fig.B1: Schematic of High Flux Backscattering instrument.

Appendix C

Instrumental Resolution

In an experiment with an ideal instrument we could measure the sample's scattering response directly. However real neutron spectrometers (and all measurement apparatus in general) have a finite resolution which tends to distort the measured distribution [C1]. The origin of the resolution distortion is due to many instrument-specific factors which lead to an accumulation of (hopefully small!) uncertainties. These uncertainties have the general effect of *blurring* the overall response. The effects of instrumental resolution often can be quantified in the *instrumental resolution function*. Mathematically, the resolution function and the intrinsic scattering function are convolved to yield the measured response. We present here an example of a convolution of two functions and the effects of the resolution width.

In this example we assume that the resolution function, $R(E)$, is a normalized Gaussian centered at zero,

$$R(E) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2}\left(\frac{E}{\sigma}\right)^2\right) \quad \text{C1}$$

and the intrinsic scattering function, $S(E)$, is a triangle function centered at zero with a base, Δ , one unit wide ($\Delta=1$) and unit height,

$$S(E) = \frac{2}{\Delta} \left[\left(E + \frac{\Delta}{2}\right) \theta\left(E + \frac{\Delta}{2}\right) - 2E\theta(E) + \left(E - \frac{\Delta}{2}\right) \theta\left(E - \frac{\Delta}{2}\right) \right] \quad \text{C2}$$

where $\theta(E)$ is the unit step function.

The measured response, $I(E)$, is given by the convolution integral,

$$I(E) = R(E) \otimes S(E) \\ = \int dE' R(E-E')S(E') \quad \text{C3}$$

where \otimes denotes the convolution operation and the integral is over all values of E' . When the Gaussian width parameter σ is small, the Gaussian approaches a delta function, and the result of the convolution looks very similar to the original triangle function. Figure C1 shows this result for a full-width at half maximum (FWHM) of 0.01. When the FWHM is larger, the resulting convolution product looks more distorted and blurred. Figure C2 shows such a case when the FWHM is 0.5.

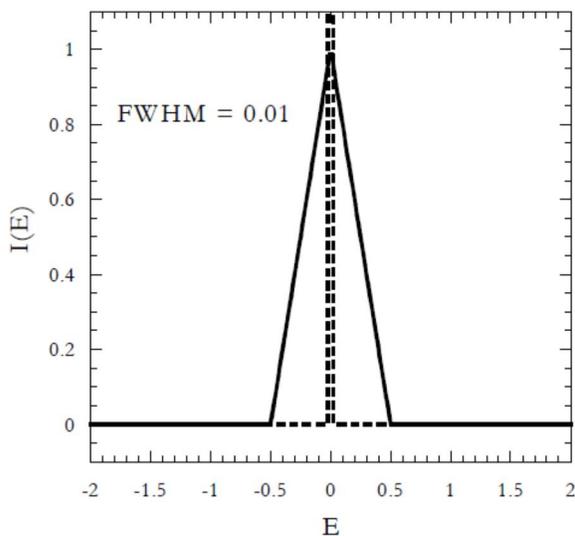


Fig. C1: Result of the convolution of the triangle function with a Gaussian of FWHM of 0.01.

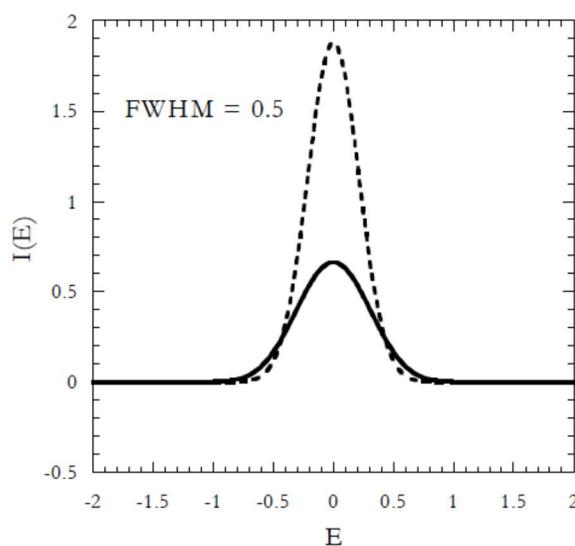


Fig. C2: Result of the convolution of the triangle function with a Gaussian of FWHM of 0.5.

Note that as $R(E)$ becomes more narrow, the convolution product looks more like $S(E)$. For a δ -function $R(E)$, the convolution product is exactly $S(E)$. Knowledge of the instrumental resolution function is essential for detailed lineshape analysis. Often this can be measured using an elastic scatterer.

In many cases, the instrumental resolution can be measured directly and used in the model fitting procedure via the convolution product. If we measure the scattering function from a purely elastic scatterer (ignoring the angular or Q -dependence for now) then the measured quantity is directly proportional to the resolution function. In particular, the elastic scattering

function can be represented by a Dirac delta function with area A : $S_{EL}(E) = A\delta(E)$. When convolved with the resolution function, we get the measured response:

$$I_{\text{meas}}(E) = A \times \delta(E) \otimes R(E) = A \times R(E) \quad \text{C4}$$

Note that we must normalize the resolution function so that it has unit area. This is necessary so that we can extract the integrated intensity of the intrinsic lineshape, $S(E)$, from the fit to the model. Since the integrated intensity of the convolution product of two functions is equal to the product of the areas of the two functions then, if one of the areas is unity (as in the case of a normalized resolution function), the other must be the total area of the measured intensity.

References

[C1]. J.T.Grissom and D.R.Koehler, *Am.J.Phys* **35**, 753 (1967).